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(54) Procedure for the removal of carbon disulfide from waste gas mixtures

(57) The present invention concerns a procedure for the removal of carbon disulfide from waste gas mixtures using a solution of alkanolamines in organic solvents.

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## Description

The present invention concerns a procedure for the removal of carbon disulfide from waste gas mixtures, using a solution of alkanolamines in organic solvents.

In spite of serious disadvantages – such as its poisonous nature and low point of flammability – carbon disulfide is an indispensable synthesis building block in the manufacture of many valuable products and is produced on a large scale in the chemical industry. Because of its poisonous nature, carbon disulfide emissions must be practically completely prevented.

Waste gases accruing in chemical processes typically consist of displacement air and process waste gases of relatively low volume flows (0 to approx. 20 m<sup>3</sup>/h), which if carbon disulfide is present in the reaction mixture, it often saturates that mixture. The procedures currently used in waste gas purification by large plants with large waste gas flows with a relatively low load (see Ullmann, Enzyklopädie der Technischen Chemie [Encyclopedia of Industrial Chemistry], 4<sup>th</sup> edition, vol. 2, pp. 609 and 614), in which carbon disulfide is adsorbed on active charcoal, can be realized here only after strong dilution. In addition, in particular the regeneration costs cannot be supported by small plants and are barely industrially realizable.

It is already known (for instance Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], 4<sup>th</sup> edition, vol. 9, p. 825) that primary or secondary amines form dithio-carbamic acids, or their salts, with carbon disulfide, in an exothermic reaction according to the following equation:



With the additional use of an auxiliary base, such as NaOH or KOH, the reaction occurs according to the following equation:



US-P 3,856,321 describes a procedure for the removal of acid components from waste gas flows using alkyl-aminoethanols and basic salts in aqueous solution. Among the acid components, carbon disulfide is also mentioned, where the patent however does not describe any implementation examples in this regard. In addition, tests have shown that especially for carbon disulfide, water is not a suitable solvent, since high degrees of washout can be achieved only using extra-long residence times in the washing column.

A suitable procedure for the removal of carbon disulfide from waste gas mixtures should be flexible in terms of the gas load, be able to handle high carbon disulfide loads in the waste gas and exhibit a high degree of washout. The absorption agents used should be readily available and lead to easy to dispose waste products. Finally the procedure should not be prone to problems and be operable at low overall costs.

It was then surprisingly found that these requirements are met very well by a procedure for the removal of carbon disulfide from waste gas mixtures, characterized by the carbon disulfide-containing waste gas being brought into contact with an absorption

liquid consisting of a solution of a (C<sub>1</sub>-C<sub>6</sub>)-alkanolamine, or a N-(C<sub>1</sub>-C<sub>4</sub>)-alkyl-(C<sub>1</sub>-C<sub>6</sub>)-alkanolamine, in an organic solvent.

Ethanolamine is a preferred alkanolamine, but especially preferred are the N-alkylated alkanolamines methyl-aminoethanol and ethyl-aminoethanol.

The preferred organic solvents are those that dissolve the dithio-carbamic acid salts generated. Among especially preferred organic solvents are (C<sub>1</sub>-C<sub>8</sub>)-alkanols, such as methanol, ethanol, the propanol, butanol and pentanol isomers, as well as 2-ethyl-hexanol, or mixtures of these alcohols, where in each case an optimum can be found between the vapor pressure that decreases with increasing molecular weight and the improved capacity to dissolve dithio-carbamate salts with decreasing molecular weight.

Other especially preferred organic solvents are furthermore glycol ethers such as diethylene glycol-dimethyl ether, triethylene glycol-dimethyl ether and tetraethylene glycol-dimethyl ether, or mixtures of them, as well as polyalkene glycols such as triethylene glycol.

The concentration of the alkanolamine in the organic solvent, in each case, can be varied within wide limits. It is advantageous here if all the reactants, in particular the salts generated, remain dissolved in the solvent, to prevent clogging of the absorption columns. An advantageous upper concentration limit is therefore established by the solubility of the dithio-carbamic acid salts. But also in those cases in which the solubility is high, preferably the solvent:amine ratio should not fall to below 1:1 (vol./vol.), especially preferred the ratio of 2:1 (vol./vol.), since otherwise the viscosity of the solution will be too high.

The temperature of the absorption solution can be varied in the range from 0°C to near the boiling point of the solution. A temperature of 20-50°C is preferred. At these temperatures the reaction rate of carbon disulfide with alkanolamine is high enough to keep the concentration of free carbon disulfide in the solution almost below the limit of detection, even for high loads.

At higher temperatures – especially if solvents of comparatively high vapor pressure are used – a downstream cold trap to condense the solvent and/or the alkanolamine can be appropriate.

It may be advantageous to add an auxiliary base to the solution of alkanolamine

and organic solvent. Among preferred auxiliary bases are NaOH and KOH, which can be used in concentrations of up to maximally the concentration of the alkanolamine (in mol/L). Higher concentrations are not harmful, but are not practical.

In a preferred industrial implementation form of the procedure according to the invention, the procedure is such that the absorption liquid is recirculated in a washer, consisting of a packed column and a container for the absorption liquid, and the carbon disulfide-containing gas is sent at countercurrent through the column.

The procedure according to the invention is not only suitable for the removal of carbon disulfide from neutral gas flows, for instance from nitrogen or air, but most especially – surprisingly – also from weakly acid gas flows, for instance hydrogen sulfide or carbon dioxide. The gases here dissolve to saturation in the absorption solution, which however does not impair its effectiveness in terms of carbon disulfide absorption.

The degree of carbon disulfide washout in the procedure according to the invention, at  $> 95\%$ , in most cases even  $> 99\%$ , is very high. It is also advantageous that it remains practically constant until close to the point of exhaustion of the absorption liquid, that is, the chemical equivalence point corresponding to the equations given above. Water contents in the solvent to up to approximately 20% do not affect the degree of washout.

The exhausted absorption liquids are advantageously sent to an incineration plant for chemical wastes.

The examples below illustrate the procedure according to the invention:

#### Example 4

In a production plant overall approximately  $16 \text{ m}^3$  of waste gas accrued over 2 h. The amount of waste gas, consisting essentially of nitrogen, varied between 3 and  $20 \text{ m}^3/\text{h}$ , the  $\text{CS}_2$  content between 0 and  $700 \text{ g/m}^3$  and the  $\text{H}_2\text{S}$  content between 0 and  $10 \text{ g/m}^3$ . The waste gas was sent in countercurrent into a column of 150 mm inner diameter, filled to a height of 80 cm with 15 mm diameter Pall rings, against a flow of  $400 \text{ L/h}$  of a wash liquid consisting of 20 L n-butanol and 10 L 2-methyl-aminoethanol. The temperature was of  $20\text{-}25^\circ\text{C}$ . The carbon disulfide was washed out of the waste gas to  $\geq 99.9\%$ .

#### Examples 2 through 4

A laboratory column filled to 30 cm with Raschig rings was loaded with nitrogen that contained approximately  $100 \text{ g CS}_2/\text{m}^3$ . The gas velocity was of  $270 \text{ m}^3/\text{m}^2 \times \text{h} = 0.075 \text{ m/sec}$ . The residence time of the gas in the column was therefore approx. 4 sec, the washing liquid in countercurrent approx.  $14.4 \text{ m}^3/\text{m}^2 \times \text{h}$ .

Example	Solvent	Amine	Solvent:amine ratio	Degree of washout	$\text{CS}_2$
2	Ethanol	2-methyl-aminoethanol	2:1	$> 99\%$	
3	n-butanol	2-methyl-aminoethanol	2:1	$> 99\%$	
4	tetraethylene glycol dimethyl ether	2-methyl-aminoethanol	2:1	$> 99\%$	

## Comparison example

Work was performed under the same conditions and with the same equipment as in Examples 2 through 4:

Solvent	= water
Amine	= 2-methyl-aminoethanol
Water:amine ratio (vol.:vol.)	= 2:1
Degree of CS <sub>2</sub> washout	= < 20%

## Examples 5 through 7

Through two 250 mL gas-washing bottles customary in a laboratory, connected in series, each filled with 200 mL absorption liquid at room temperature, was sent a gas stream for 75 min, at approx. 50 L/h, consisting of 88% H<sub>2</sub>S and 12% CS<sub>2</sub> (total amount 2.4 mol H<sub>2</sub>S and 0.15 mol CS<sub>2</sub>). The degree of CS<sub>2</sub> washout was determined.

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Example	Solvent	Amine	Auxiliary base	Degree of CS <sub>2</sub> washout
5	90% ethanol	2 x 100 mmol 2-ethylamino ethanol	2 x 100 mmol NaOH	> 99%
6	80% ethanol	2 x 100 mmol 2-ethylamino ethanol	2 x 100 mmol NaOH	> 99%
7	Methanol	2 x 100 mmol 2-ethylamino ethanol	2 x 100 mmol NaOH	> 99%

## Example 8

38 g of a gas mixture consisting of 70% H<sub>2</sub>S (0.8 mol) and 30% CS<sub>2</sub> vapor (0.15 mol) were sent through a 30 cm laboratory column filled with Raschig rings of approx. 3 cm inner diameter; into this column was recirculated a solution of 30 g (0.4 mol) ethanolamine in 200 mL ethanol, at 17 L/h, in the course of 1 ½ h. The degree of washout of CS<sub>2</sub> was > 96%.

## Example 9

In the equipment of Example 8, a solution of 30 g (0.4 mol) of 2-methyl-aminoethanol in 200 mL ethanol was recirculated. Over a period of 1 ½ h, 57 g of a gas mixture consisting of 80% CO<sub>2</sub> (1 mol) and 20% CS<sub>2</sub> vapor were sent through the column. The degree of washout of CS<sub>2</sub> was of > 96%.

**Patent claims**

1. Procedure for the removal of carbon disulfide from waste gas mixtures, **characterized by** the CS<sub>2</sub>-containing waste gas being brought into contact with an absorption liquid consisting of a (C<sub>1</sub>-C<sub>6</sub>)-alkanolamine, or a N-(C<sub>1</sub>-C<sub>4</sub>)-alkyl-(C<sub>1</sub>-C<sub>6</sub>)-alkanolamine in an organic solvent.
2. Procedure according to claim 1, **characterized by** the alkanolamine used being ethanolamine, methyl-aminoethanol or ethyl-aminoethanol.
3. Procedure according to claim 1 and/or 2, **characterized by** the organic solvent used being (C<sub>1</sub>-C<sub>8</sub>)-alkanoles, glycol ethers or polyalkene glycols.
4. Procedure according to one or more of the claims 1 through 3, **characterized by** the temperature of the absorption liquid being of 20-50°C.
5. Procedure according to one or more of the claims 1 through 4, **characterized by** the ratio of solvent to amine in the absorption liquid not falling below 1:1 (vol./vol.).
6. Procedure according to one or more of the claims 1 through 4, **characterized by** the ratio of solvent to amine in the absorption liquid not falling below 2:1 (vol./vol.).
7. Procedure according to one or more of the claims 1 through 6, **characterized by** an auxiliary base being added to the absorption liquid.
8. Procedure according to one or more of the claims 1 through 7, **characterized by** the absorption liquid being recirculated in a washer, consisting of a packed column and a container for the absorption liquid, and by the CS<sub>2</sub>-containing gas moving in countercurrent through the column.